PEER REVIEW OF THE SAPRC-07 CHEMICAL MECHANISM: RESPONSE TO REVIEWERS' COMMENTS

Prepared for
California Air Resources Board Contract 07-730

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March 20, 2009

Summary

Because of its intended use in regulatory applications, the California Air Resources Board contracted for peer reviews to be carried out on the SAPRC-07 chemical mechanism that was recently developed by the author. The reviewers were internationally recognized scientists representing various areas of relevant expertise and consisted of R.G. Derwent, M.E. Jenkin and M. J. Pilling of the U.K, M. Azzi, S. White and D. Angove of CSIRO in Australia, R. Harley of U.C. Berkley, and W. R. Stockwell of Howard University. A brief summary of the four reviews is as follows, and more detailed discussions of each are given in separate sections below.

The review of Derwent et al. (2008) focused on comparing incremental ozone impacts of 121 selected compounds calculated using SAPRC-07 and the Master Chemical Mechanism (MCM v 3.1. Their general conclusion was that for most compounds the ozone impacts calculated using the two mechanisms were consistent with each other, though there were significant differences for certain compounds. It is unclear which mechanism is more accurate for these compounds, and we conclude that the data do not clearly indicate any case where we need to change SAPRC-07 at this time.

The review of Azzi et al. (2008) focused on comparing the ability of the SAPRC-07 mechanism, and also SAPRC-99 and MCM 3.1, to simulate the results of isoprene, toluene, m-xylene, and evaporated fuel environmental chamber experiments carried out in the CSIRO chamber. These experiments were not previously used to evaluate these mechanisms. In general, SAPRC-07 performed reasonably well in simulating these data given the uncertainties. There is some indication of problems with the toluene mechanism that merits further investigation, though overall the results are not sufficient to indicate it is appropriate to change the toluene mechanism at this time.

The review of Harley (2009) discussed implementing the mechanism in 3-D modeling, and brings up several important issues concerning the mechanism that need to be addressed. These include the need to develop a version of the mechanism that can be used for sensitivity studies on the uncertain and important OH + NO_2 rate constant, and the need to update the base ROG mixture used to derive the fixed parameter version of the mechanism. Although it is not feasible to modify the mechanism at the present time to incorporate these recommendations, this work should be given priority for future efforts.

Stockwell (2009) gives a detailed comparison of the individual chemical reactions and rate constants in the SAPRC-99, RACM2, and CB05 mechanisms and comments on differences and his

assessment of their chemical reasonableness and the extent to which they represent the state of the science. Overall, he concludes that SAPRC-07 represents the current state of the science and he is complementary about certain aspects of the mechanism, but he had several criticisms and recommendations. Although we do not agree with all of his comments, in two cases his comments lead to our making changes to the mechanism.

As a result of Stockwell's peer review discussed above and also errors discovered recently during the process of expanding the mechanism for the EPA, it was found to be necessary to make some corrections to the SAPRC-07 mechanism before it, and its reactivity scale, is finalized for regulatory applications. These are summarized in this report and are incorporated in a revised version of the SAPRC-07 mechanism documentation report (Carter, 2009) that is available at the SAPRC mechanism web site at http://www.cert.ucr.edu/~carter/SAPRC. The environmental chamber data were re-evaluated using this revised mechanism and the MIR and other reactivity scales were recalculated and are given in the revised documentation report (Carter, 2009). The modifications did not result in any significant changes to the fits to the chamber data and there was no need to change any of the adjustable parameters for any compounds. These reactivity scale changes were minor in the MIR scale (less than 4% for all compounds) but in a few cases there were changes of up to 30% in the lower NO_x scales because the affected reactions are more important in low NO_x conditions.

The author wishes to thank the CARB for arranging this peer review and the peer reviewers for their helpful comments.

Derwent et al. (2008) Review

The review of Derwent et al. (2008) focused on comparing incremental ozone impacts of selected compounds calculated using SAPRC-07 and the Master Chemical Mechanism (MCM v 3.1) developed by Jenkin et al (1997, 2003) and Saunders et al (2003). MCM 3.1 is the most comparable mechanism to SAPRC in terms of its ability to separately represent different VOCs and representing the current state of the science, though different approaches are used in terms of level of detail and mechanism development approaches. Ozone impacts of a total of 121 compounds, listed on Table 1, were calculated, representing a variety of types of structures. The MCM reactivity calculations were carried out with a subset of the maximum incremental reactivity (MIR) scenarios used by to derive the SAPRC-07 MIR scale, specifically the "averaged conditions" scenario and the four city-specific scenarios named after various cities in California (Carter, 1994a,b). These were compared to MIR values tabulated in the SAPRC-07 documentation report (Carter, 2008a), which were calculated using 39 MIR scenarios named after various cities throughout the United States[1].

The reactivity results reported for the MCM are quantified as POCP values, which are defined as incremental reactivities relative to ethylene = 100. Table 1 lists the average and standard deviation of the POCP values calculated using the MCM mechanism for the five selected MIR scenarios. In order to place the SAPRC-07 results on the same basis as those reported for MCM, we, we calculated POCP values (i.e., incremental reactivities relative to ethene=100) for the same 5 selected scenarios, and their averages and standard deviations are also listed on Table 1. A comparison of the reactivities relative to ethene calculated using the different mechanism is given in Figure 1, which plots those calculated using MCM against those calculated using SAPRC-07, and shows the 1:1 line where all the points should fall if the two mechanisms gave the same results.

[1] Note that since these scenarios are seriously out-of-date they do not actually represent the current conditions of the cities after which they are named, though as a set they represent a variety of conditions that may be appropriate for deriving general scales.

Table 1. Comparison of POCP's (Incremental reactivities relative to ethene=100) for selected compounds calculated using the SAPRC-07 and MCM 3.1 mechanism for selected MIR box model scenarios.

Compound	SAPRC-07		MCM 3.1		Diff	Note
	POCP	Sdev	POCP	Sdev	[a]	[b]
ethane	2.5	0.5	3.0	1.0	-	
propane	4.5	0.6	9.0	2.0	-	
butane	10	2	18	4	-	
pentane	12	2	22	5	-	
hexane	11	2	20	4	-	
heptane	9	2	15	4	-	
octane	7	2	13	5	-	
nonane	6	2	11	6	-	
decane	4.8	1.5	12.0	7.0	-	
undecane	4.0	1.4	12.0	7.0	-	
dodecane	3.5	1.4	12.0	8.0	-	
i-butane	12	1	20	4	-	
neopentane	7	1	10	2	-	
i-pentane	13	2	21	4	-	
2,2-dimethylbutane	11	1	13	2	-	
2,3-dimethylbutane	9	1	20	3	2.2	
2-methylpentane	13	2	26	5	-	
3-methylpentane	16	3	25	5	-	
2-methylhexane	10	2	19	4	-	
3-methylhexane	14	2	24	5	-	
cyclohexane	11	3	20	5	-	
ethylene	100	0	100	0	-	
propylene	132	4	134	14	-	
but-1-ene	106	3	108	17	-	
1-pentene	78	3	89	15	-	
3-methylbut-1-ene	75	3	89	17	-	
hex-1-ene	57	3	92	13	1.6	
butylene	73	7	97	12	-	
2-methylbut-1-ene	73	5	92	10	-	
cis-but-2-ene	161	11	165	33	-	
trans-but-2-ene	172	13	173	35	-	
2-methylbut-2-ene	161	19	155	35	-	
cis-pent-2-ene	113	5	145	32	-	
trans-pent-2-ene	116	5	145	31	-	
cis-hex-2-ene	90	4	127	30	-	
trans-hex-2-ene	94	4	127	30	-	
1,3-butadiene	142	6	120	12	-	
isoprene	119	6	173	19	1.5	1
alpha-pinene	48	4	109	20	2.3	
beta-pinene	37	2	70	16	-	
limonene	47	4	134	31	2.8	
styrene	18	1	7	31	-	

Table 1 (continued)

Compound	SAPRC-07 POCP	SAPRC-07 Sdev	MCM 3.1 POCP	MCM 3.1 Sdev	Diff [a]	Note [b]
benzene	7	1	1	6	-	
toluene	43	3	33	8	-	
ethylbenzene	32	2	36	9	-	
propylbenzene	21	2	26	6	-	
i-propylbenzene	26	2	29	6	-	
m-xylene	115	6	94	23	-	
o-xylene	86	3	79	19	-	
p-xylene	65	2	74	17	-	
m-ethyltoluene	85	4	82	19	-	
o-ethyltoluene	62	3	65	18	-	
p-ethyltoluene	49	2	60	16	-	
1-methyl-3-i-propylbenzene	83	4	151	44	-	
1,2,3-trimethylbenzene	143	9	125	32	-	
1,2,4-trimethylbenzene	104	5	137	27	-	
1,3,5-trimethylbenzene	143	12	141	23	-	
3,5-dimethylethylbenzene	122	10	134	24	-	
1,2,4,5-tetramethylbenzene	110	7	181	47	-	
1,2,3,5-tetramethylbenzene	110	7	188	49	-	
3,5-diethyltoluene	107	9	121	25	-	
acetylene	11	0	4	0	2.6	2
propyne	74	5	101	40	-	
methanol	7	0	8	1	-	
ethanol	14	2	17	5	-	
i-propanol	6	1	13	2	2.1	
propanol	24	4	30	6	-	
i-butanol	25	3	34	2	-	
butanol	28	4	35	8	-	
sec-butanol	13	2	26	5	-	
3-methyl-1-butanol	32	3	47	3	1.5	
cyclohexanol	19	4	45	10	-	3
ethylene glycol	31	3	25	5	-	
propylene glycol	26	2	29	7	-	
dimethylether	8	1	18	5	-	
diethylether	40	2	53	9	-	
di-i-propylether	39	2	41	8	-	
2-methoxyethanol	31	1	34	3	-	
1-methoxy-2-propanol	25	3	32	6	-	
2-ethoxyethanol	39	2	42	5	-	
2-butoxyethanol	30	2	38	7	-	
methyl formate	0.5	0.1	1.0	0.0	1.8	
methyl acetate	0.7	0.1	3.0	1.0	4.5	3
ethyl acetate	6	1	11	2	-	
i-propyl acetate	11	1	16	3	-	
n-propyl acetate	7	1	15	3	-	
butyl acetate	7	1	14	2	-	

Table 1 (continued)

Compound	SAPRC-07 POCP	SAPRC-07 Sdev	MCM 3.1 POCP	MCM 3.1 Sdev	Diff [a]	Note [b]
formic acid	0.6	0.1	1.0	0.0	1.6	
acetic acid	7	1	6	1	-	
propanoic acid	12	2	6	2	-	
formaldehyde	119	11	78	20	-	
acetaldehyde	72	2	59	20	-	
propionaldehyde	75	4	63	24	-	
i-butyraldehyde	56	3	60	18	-	
butyraldehyde	63	3	60	21	-	
3-methylbutanal	53	2	73	23	-	
pentanal	53	3	74	20	-	
glyoxal	160	20	60	16	2.7	2
methylglyoxal	209	27	163	44	-	
acrolein	81	6	80	44	-	
methacrolein	67	3	136	41	-	1
benzaldehyde	-10	2	-36	34	-	
4-methylbenzaldehyde	-9	2	-36	43	-	
2-methylbenzaldehyde	-9	2	-101	83	-	
3-methylbenzaldehyde	-9	2	-83	69	-	
acetone	3.8	0.3	4.0	1.0	-	
methylethylketone	15	1	18	4	-	
diethylketone	12	2	17	5	-	
cyclohexanone	12	2	21	5	-	
methyl-i-butylketone	41	2	53	6	-	
diacetone alcohol	6	1	21	3	3.7	4
phenol	31	2	-119	166	-	
o-cresol	27	2	-20	116	-	
2,4-xylenol	24	2	52	95	-	
2,5-xylenol	24	2	42	115	-	
2,3-xylenol	24	2	16	105	-	
methylene dichloride	0.4	0.1	1.0	1.0	-	
ethyl chloride	2.6	0.5	12.0	5.0	-	5
ethylidene dichloride	17	2	91	22	5.4	4,6
trichloroethylene	6	1	14	3	2.3	7
tetrachloroethylene	0.3	0.0	1.0	0.0	3.7	6

[a] Ratio of higher to lower POCP's for compounds whose POCP's differed by more than two standard deviations from each other.

[b] Notes discussing possible sources of differences are as follows:

1 MCM has higher photolysis rates for photolysis of some of the major products of isoprene. For methacrolein, MCM photolysis rate for zero zenith angle is larger by approximately a factor of 3.

Table 1 (continued)

2	MCM has a lower photolysis rate for glyoxal, the major product formed from acetylene. The photolysis rate difference for zero zenith angle is approximately a factor of 4.
3	MCM predicts the formation of more reactive products for these compounds.
4	It is possible that MCM is using different structures for these compounds than SAPRC-07. Compound with these names could not be found on the MCM web site.
5	MCM has exactly the opposite branching ratio for the initial two reactions than SAPRC-07. This results in different reactivity products being predicted. The SAPRC-07 branching ratio was calculated using structure-reactivity methods that are used for other compounds.
6	This compound is predicted to form phosgene as a major product. Phosgene is treated as inert in SAPRC-07 but is assumed to photolyze with the same rate as standard aldehydes in MCM.
7	The products formed appear to be more photoreactive in MCM than SAPRC-07.

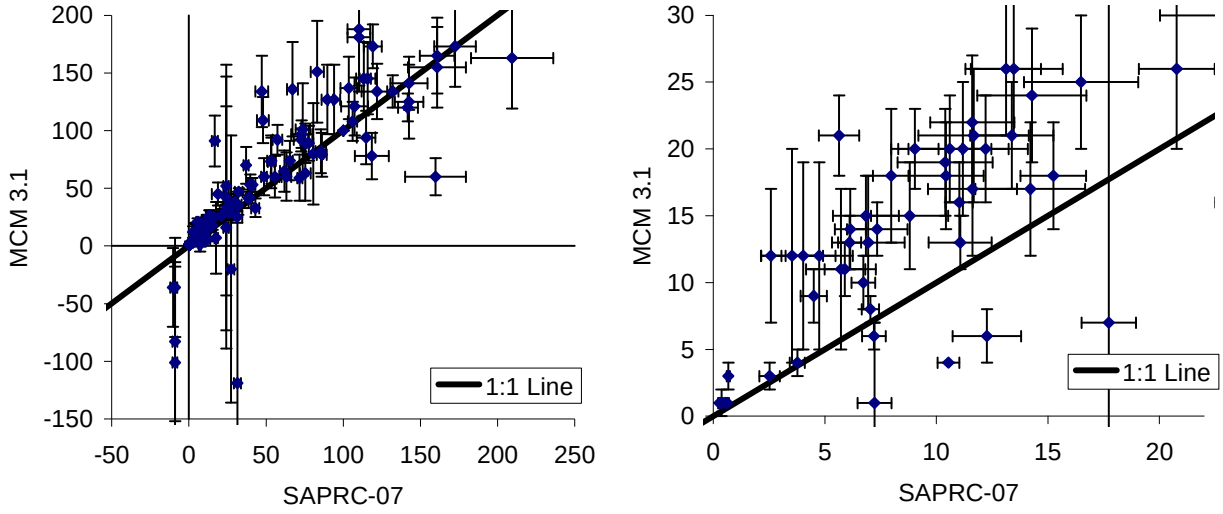

Figure 1. Plots of average incremental reactivities relative to ethylene = 100 calculated using the MCM 3.1 mechanism against those calculated using SAPRC-07 for five selected MIR box model scenarios.

Note that the SAPRC-07 reactivity values given in Table 1 and Figure 1 are somewhat different than the SAPRC-07 reactivities used for comparison in the Derwent et al. (2008) report, which compared the MCM POCP's with absolute tabulated MIRs, and used linear regressions for each class of compound to determine consistency. We believe that comparing POCPs (reactivities relative to ethylene) directly is more useful since if the mechanisms are consistent then the absolute, as well as the relative, values should also be the same. Thus it is not necessary to carry out separate regressions for each class of compounds. Despite the differences in approach in our analysis using the data of Derwent et al. (2008), the general conclusions are the same in terms of consistencies between the mechanisms.

As noted by Derwent et al. (2008), in general the two mechanisms gave consistent results, though there were differences for some compounds that were well outside the variability from scenario to scenario. Table 1 shows the ratios of POCP values for those compounds where the difference was more than twice the combined standard deviations of the two calculations. These are generally the same outlier compounds noted by Derwent et al. (2008), though as noted above the comparison method is slightly different. Although this was not evident from the Derwent et al (2008) report because of their comparison method, the left plot on Figure 1 suggests that for moderately reactive compounds there is a general tendency for the reactivities relative to ethylene to be higher for MCM than for SAPRC-07. This may be due to differences in the base mechanism or mechanisms used for common reactive products that might be worth investigating

Derwent et al. (2008) noted that the differences reflected different approaches taken and assumptions made during the derivation of mechanisms of individual compounds, and they make no conclusions as to which representation is better. They reported no cases where they believed that the SAPRC-07 mechanism had an error that needed to corrected at this time, though they noted that there are many cases where more data are needed to resolve the differences and determine which approach is more appropriate. Generally, we agree with their conclusions in this regard.

However, the possibility that some of the differences may be due to errors in the SAPRC-07 mechanism that need to be corrected cannot be ruled out. In order to investigate this, we went to the MCM web site at http://mcm.leeds.ac.uk/MCM/ to determine how the MCM mechanism for some of the outlier compounds differed from SAPRC-07. Some cases were found where there were clear differences between the mechanism that might account for the discrepancies, and these are noted in footnotes to Table 1. In all those cases we believe our estimates are appropriate (or otherwise we would have made different estimates at the time the mechanisms were developed) and we do not believe there is a need to change the SAPRC-07 at this time, though in most cases the MCM are reasonable alternatives and cannot be ruled out either. As noted by Derwent et al. (2008), they represented differing approaches and assumptions, and do not indicate necessarily errors in SAPRC-07 that need to be corrected at this time.

Table 1 also indicates compounds with significantly different POCP values where we did not investigate or could not elucidate the causes of the differences between the mechanisms. For example, the MCM predicts significantly higher ozone impacts for the terpenes than SAPRC-07, but the MCM terpene mechanisms are too complex to clearly elucidate the differences in a reasonable amount of time. However, it should be noted that the SAPRC-07 mechanisms for a number of terpenes have evaluated against chamber data, so even if they are incorrect in some details they are unlikely to have very large errors in reactivity predictions. This is also the case for some other compounds where differences between the mechanisms were found.

To conclude, we believe that the review of Derwent et al. (2008) has provided a valuable comparison of reactivity predictions of the different mechanisms, and cases where more data and mechanism comparison work is needed were found. However, the results to date do not indicate any need to correct or modify the SAPRC-07 mechanism for any compound at this time.

Azzi at al. (2008) Review

The review of Azzi et al. (2008) focused on comparing the ability of the SAPRC-07 mechanism, and also SAPRC-99 and MCM 3.1, to simulate the results of CSIRO environmental chamber experiments that were not previously used in the development and evaluation of these mechanisms. These consisted of m-xylene - NO_x, toluene - NO_x, and isoprene - NO_x irradiations, and irradiations of NO_x with wholly or partially evaporated motor fuel. The ability of the mechanisms to simulate O_3 formation, NO oxidation and reactant VOC consumption were evaluated. The model simulations used appropriate representations of chamber effects, using procedures and assumptions similar to or based on those we used when evaluating SAPRC and other mechanisms with other chamber data.

Generally the SAPRC-07 mechanism preformed satisfactorily in simulating the m-xylene experiments, and also performed better than the other two mechanisms evaluated. Therefore, no need to modify the SAPRC-07 m-xylene mechanism is indicated by this work.

The performance was not quite as good in simulating the isoprene experiments, though it was comparable to the other two mechanisms, and the fits to the data were within the variability observed when evaluating the isoprene mechanism against the larger UCR chamber dataset used in the initial evaluation of the mechanism (Carter, 2008a). In particular, the performance in simulating these isoprene experiments, as well as the UCR chamber dataset used previously, was not such that modifying the mechanism to improve the performance is not appropriate at this time.

The performance of all three mechanisms in simulating the results of the three CSIRO toluene - NO_x experiments was quite poor, with the rate and amount of ozone formation during the middle stage of the experiments being significantly underpredicted. The differences between the three mechanisms were small compared to the differences between the mechanisms and the data, though generally SAPRC-07 was the least bad of the three. A typical result is shown in Figure 2a, which shows experimental and calculated data for ozone for a representative run.

This poor performance in simulating the CSIRO toluene experiments contrasts with the results of the SAPRC mechanism evaluation against UCR and TVA toluene - NO_x chamber data using a variety of chambers, where generally good fits for both SAPRC-99 and SAPRC-07 are observed (Carter, 2008a, 2009). This is shown in Figure 2b, which shows plots of model errors in the simulations of a large number of UCR and TVA chamber experiments, and shows that the final ozone levels were simulated with relatively little bias in these datasets, though there was run-to-run variability (Carter, 2008a, 2009). The reason for the different results in the new CSIRO experiments is unknown, and may indicate a problem with the mechanisms that are not evident when modeling the other chamber runs. However given the larger number of UCR experiments and the similarly good results with the experiments in the TVA chamber, we believe the data from the new CSIRO chamber runs are not sufficient to indicate a need to change the toluene mechanism at this time. This problem clearly needs to be investigated, however, especially since, as discussed in the SAPRC-07 documentation report, not all of the available UCR toluene chamber data are satisfactorily simulated in all respects (Carter, 2008a, 2009).

Azzi et al. (2008) also show results of model simulations of several evaporated fuel - NO_x irradiation experiments. Such experiments are valuable for verification of mechanisms for more atmospherically realistic complex mixtures but are less useful for mechanism development and detailed evaluation. This is because poor performance could be attributed to uncertainties in characterizing the complex mixtures, and because of the many compounds it is difficult to determine which aspect of the mechanism is causing any problems. Also, with complex mixtures there is a greater chance that compensating errors could be causing good model performance for the wrong reasons.

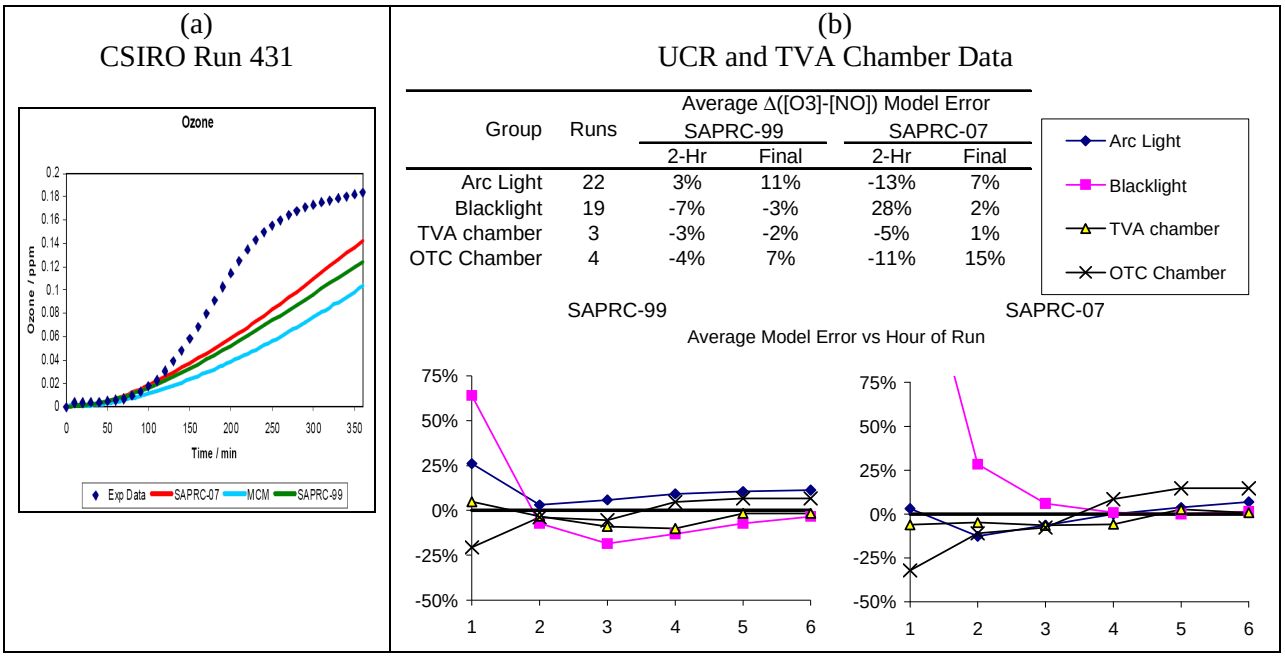

Figure 2. Comparison of model performance in simulations of toluene - NO_x environmental chamber data. (a) Experimental and calculated ozone data for a representative CSIRO run as given in the report of Azzi et al. (2008) (b) Plots of average model errors against hour of run for the UCR and TVA toluene - NO_x experiments used when evaluating SAPRC-07 (from Carter, 2009).

Both SAPRC-99 and SAPRC-07 simulated the results of the headspace fuel injection experiments reasonably well, though SAPRC-99 predicted somewhat more ozone and predicted the ozone in one of the runs somewhat better. MCM predicted lower ozone in those experiments and did not simulate the data as well. However, for the complete fuel injection runs, SAPRC-99 predicted significantly more ozone than SAPRC-07 and simulated the data much better, and MCM predicted lower ozone than SAPRC-99 but more than SAPRC-07. It is unclear why there would be so much difference between SAPRC-99 and SAPRC-07 for one type of experiment compared to the other, and why SAPRC-07 would predict more ozone than MCM in one case and less in the other. The evaluation against the large database of UCR chamber experiments does not indicate significant differences between SAPRC-99 and SAPRC-07 in simulating complex mixture experiments. We suspect that the differences between SAPRC-99 and SAPRC-07 in the simulations of the whole fuel experiments may be due to problems with representing the mixtures when simulating the experiments, and we would need to see this ruled out before concluding that these results indicate any problems with SAPRC-07 that needs to be addressed.

To conclude, the work described by Azzi at al. (2008) provide a useful independent evaluation of the SAPRC (and MCM) mechanisms against an environmental chamber data set that was not used in their development. With the possible exception of the simulation of the toluene experiments, the results are generally within the run to run variability observed when simulating the various chamber experiments, and do not indicate any need to modify SAPRC-07. The simulations of the toluene experiments suggest possible problems with the toluene mechanism, but are not sufficient in themselves to serve as a basis for modifying the mechanism given its satisfactory performance in simulating the much larger database used in its development.

Harley (2009) Review

The review of Harley (2009) discussed implementing the mechanism in 3-D modeling, changes in model predictions relevant to SAPRC-99 and the issue of the OH + NO_2 rate constant, and VOC lumping and emissions processing issues, and made several specific recommendations. These are discussed below.

A condensed version of SAPRC-07, designated CS07A (Carter, 2008b) was implemented into a 3-D model to simulate an ozone episode in the California South Coast Air Basin, and its predictions were compared with those of SAPRC-99. Although CS07A is not exactly the same as the full SAPRC-07 mechanism discussed by the other reviewers and used to calculate the reactivity scale, its ozone predictions were shown to be essentially the same as full SAPRC-07 under a wide variety of conditions (Carter, 2008b) and the results would probably been very close had the full SAPRC-07 mechanism been used. As expected, the condensed mechanism was found to require less computer time because of its smaller size. CS07A was also found to form somewhat less ozone and somewhat HNO_3 than SAPRC-99, and this is attributed to the 19% increase in the OH + NO_2 rate constant in SAPRC-07 relative to SAPRC-99, though the possibility that other differences in the mechanisms could be influencing this could not be ruled out. The full SAPRC-07 mechanism has the same rate constant for this and the other major ozone formation reactions and would be expected to give similar results.

Previous sensitivity studies have shown that the OH + NO_2 rate constant is very important in affecting ozone predictions, and sensitivity + uncertainty analyses have identified it as a major issue in airshed modeling. The 19% increase in the rate constant implemented in SAPRC-07 results from changes in recommendations of both the latest IUPAC (2006) and NASA (2006) reviews, which are used as the basis for most of the rate constants in the base inorganic mechanism. However, an unpublished report of Okumura et al (2005) cited by Harley (2009) and an presentation given by Sander at the recent Atmospheric Chemical Mechanism meeting (Sander, 2008) suggest that use of a lower rate constant, closer to that used by SAPRC-99, may be more appropriate, based on new data and analyses that take into account the formation of a possible HOONO intermediate in the measurement systems. However, the evaluations of IUPAC (2006) and NASA (2006) both discuss the possible involvement of HOONO, so possible complications caused by this intermediate were also taken into account when they made their recommendations. Since the evaluations of NASA and IUPAC have not been revised and the data of Okumura and Sander have not been published[2], and since we do not feel qualified to conduct an independent evaluation of this complex reaction, we do not believe it is appropriate to change this rate constant at this time.

In fact, Harley (2009) does not recommend that the OH + NO_2 rate constant be changed in the SAPRC-07 mechanism at this time. However, he does recommend that a version of the mechanism utilizing the lower rate constant be developed, so it can be used for sensitivity studies. We believe that this would be beneficial and such a mechanism would be useful for uncertainty and policy analyses, and could serve as a basis for an updated mechanism should future evaluations recommend use of a lower rate constant. However, this is a significant effort because it requires re-evaluating all the chamber data with new chamber effects parameters[3], and it may require re-deriving some mechanisms that were adjusted to fit chamber data. Therefore, this could not be done in time frame needed to respond to this review. This task could be included as part of our ongoing mechanism development and implementation projects with the CARB or the EPA if desired by these agencies. Alternatively, this could wait until the next release of the NASA and/or IUPAC evaluations, at which time the mechanism can be updated completely to these

[2] The Sander, 2008, presentation is not included among those available on the conference proceedings web site at http://airquality.ucdavis.edu/pages/events/2008/acm.htm

[3] Chamber effects parameters related to background radical sources are derived by modeling characterization experiments whose results are also sensitive to the OH + NO_2 rate constant.

evaluations if they indeed indicate use of significantly different OH + NO_2 rate parameters. At present it is not obvious what exact OH + NO_2 rate constant parameters should be used in the mechanism developed for sensitivity studies.

A separate and also important issue discussed by Harley (2009) concerns the definitions of the lumped organic species in SAPRC-07. Harley notes that the fixed parameter version of the mechanism will be much more widely used than any adjustable parameter versions, so the base ROG mixture used to derive the mechanism is important. Harley gives a number of criticisms of the base ROG mixture used to derive fixed-parameter SAPRC-07 and CS07, most if not all of which are probably valid. However, updating the base ROG mixture is beyond the scope of this project and cannot be done in the time frame required for the finalization of the SAPRC-07 mechanism for regulatory use. We understand that the CARB is initiating a project to update the base ROG mixture, and when this is available then a new version of fixed parameter SAPRC-07 and CS07 can be developed at that time.

Harley (2009) does make two recommendations regarding VOC lumping that could be made at this time if appropriate. First, he recommends that the minor species be omitted when deriving some lumped groups such as ALK5 for simplicity. However, this will require some effort and not really improve the mechanism, so at this point it is probably better not to make changes until a new base ROG mixture is available and adopted. The suggestion to exclude minor compounds could be considered at that time. More substantively, he recommends that the OH rate constant used to define the dividing line between OLE1 and OLE2 be increased slightly so that isobutene would be lumped with 1-butene (as OLE1) because these compounds are difficult to separate in GC analyses of ambient air. However, the mechanism parameters for these two compounds are different, and lumping them together would not eliminate the effect of the analysis problem because their relative contributions would affect the parameters derived for OLE1. We believe that it is more appropriate to continue to represent isobutene by OLE because its rate constant is closer to that of OLE2 than OLE1.

Harley (2009) makes two comments of an editorial nature, indicating that we give an incorrect percentage change for the OH + NO_2 rate constant relative to SAPRC-99 and use inconsistent rate constant units in Table 17. Since we are revising the SAPRC-07 documentation report as a result of considerations discussed below, these comments were addressed in the revised version of the report (Carter, 2009). However, contrary to the recommendation of Harley (2009) the rate constant units in Table 17 were changed to cm^3 $molec^{-1}$ s^{-1} to be consistent with the rate constant units used elsewhere in the report.

To summarize, Harley (2009) brings up several valid issues concerning the mechanism that need to be addressed, specifically the need to develop a version of the mechanism that can be used to conduct sensitivity studies on the uncertain and important OH + NO_2 rate constant, and the need to update the base ROG mixture used to derive the fixed parameter version of the mechanism. However, it is not feasible to modify the mechanism at the present time to incorporate these recommendations, and this work will have to be carried out in the future.

Stockewll (2009) Review

Stockwell (2009) gives a detailed comparison of the individual chemical reactions and rate constants in the SAPRC-99, RACM2, and CB05 mechanisms and comments on differences and his assessment of their chemical reasonableness and the extent to which they represent the state of the science. Overall, he concludes that SAPRC-07 represents the current state of the science and he is complementary about certain aspects of the mechanism, such as the operator approach used to represent peroxy radical reactions, and the representation of chlorine reactions. However, he does question some specific aspects of the mechanism and made a comment that resulted in our finding one error in the

mechanism that had to be corrected. The recommendations and specific comments that might be interpreted as problems Stockwell had with the mechanism are summarized below in the order they appear in his report.

Stockwell states that SAPRC-07 treats HCl as unreactive and questions the appropriateness of this when used in aerosol models. However, the mechanism does include the OH + HCl reaction, so it is not treated as unreactive.

Stockwell recommends SAPRC-07 include more detailed treatment of alcohols, with more explicit alcohol species such as used in RACM2. However, a benefit of the SAPRC mechanisms is that they have an associated detailed mechanism that has explicit reactions of these and many other individual VOCs that can be added as needed for the various modeling applications as appropriate. For example, we are developing a version of SAPRC-07 with more individual explicit species as needed for toxics modeling. The current level of detail in the fixed parameter version of SAPRC-07 is consistent with that in SAPRC-99 and appears to represent the needs of the CARB, who funded its development. Indeed, most modelers (such as Harley, discussed above) may be more interested in the more condensed versions of SAPRC-07 that include fewer, not more, explicit species.

Stockwell criticized the lumping of O_2 and N_2 with "M" in SAPRC-07 when computing the quenching reaction for O^1D in air because they have slightly different temperature dependences. However, the temperature dependence for the O^1D + M was derived to give the same rate total constants as using the two reactions with their separate temperature dependences over a range of temperatures where the model will be applied, so we do not believe that this is not an important approximation.

Stockwell made the comment that SAPRC-07 used a "different representation" for the rate constant for the $HO_2 + O_3$ reaction than does CB05 or RACM2. In fact, as a result of this comment it was found that SAPRC-07 had an apparent typographical error in the activation energy of this reaction, and correcting it resulted in a 20% increase in the 300^{o}K rate constant. Because of this, the base SAPRC-07 mechanism had to be corrected. The changes made the mechanism and its associated documentation as a result of this review and other considerations are discussed in the following section. This reaction is probably not important under the relatively high NO_x conditions used to calculate the MIR scale, but may affect model simulations in the lower NO_x scenarios.

Stockwell stated that the rate constant for methyl peroxy + NO used by SAPRC-07 is only 2/3 that used by SAPRC-07 (sic) and RACM2. Presumably he meant CB05 and RACM2. The difference is because SAPRC-07 uses the IUPAC (2006) recommendation for the temperature dependence of this reaction, while the other two mechanisms apparently use NASA (2006). However, contrary to what Stockwell states, the rate constants at 298^{o}K are about the same.

Stockwell notes that the HO_2 + formaldehyde reactions as incorporated in SAPRC-07 and CB05 are unimportant under realistic atmospheric conditions and can be removed to save computational resources. In fact he is correct. A detailed examination shows that the net effect of these reactions as implemented in SAPRC-07 are almost always negligible. The mechanism has the reaction forming an adduct that either decomposes unimolecularly back to reactants, resulting in no net reaction, or reacts with NO to form other products. The rate constants used for these reactions are such that for a net reaction to occur the NO levels would have to be so high that HO_2 would be suppressed so low that reaction of formaldehyde with HO_2 would be negligible compared to competing reactions. Since we had to modify SAPRC-07 anyway to correct the error in the $HO_2 + O_3$ rate constant, this reaction was removed. This has the advantage of removing one steady state species from the mechanism, which would have an impact on computational time for models that use solvers that don't implement the steady state approximation.

Stockwell notes that SAPRC-07 includes reactions of O^3P reactions with alkenes, which are probably not significant under most atmospheric conditions and are excluded from RACM2. However, in addition to being non-negligible in some chamber experiments, they may also be non-negligible in some high NO_x atmospheric plumes, and may be appropriate to use in models that have plume-in-grid representations.

Stockwell's report goes into considerable detail concerning other reactions in the mechanisms but in most cases does not include criticisms of SAPRC-07 that need to be addressed. Because of time constraints, we did not go through all the reactions listed in the Appendix to his report, but considered only aspects of his discussion in the main report that can be interpreted as recommendations or criticisms.

To summarize, Stockwell (2009) concludes that SAPRC-07 represents the current state of the science and overall his report is more complementary than critical. He does note a few discrepancies with the other mechanisms and has some criticisms and recommendations, but in most cases we do not believe that changes are needed. However, there were two cases where Stockwell's comments have resulted in changes being made to the SAPRC-07 mechanism. These are discussed in the following section.

Mechanism Revisions

As a result of Stockwell's peer review discussed above and also errors discovered recently during the process of expanding the mechanism for the EPA, it was found to be necessary to make some corrections to the base SAPRC-07 mechanism before it, and its reactivity scale, is finalized for California regulatory applications. The modifications that were made are summarized below. The first two modifications were made as a result of Stockwell's review and the rest were made as a result of problems discovered independently.

- An error in the activation energy for the $HO_2 + O_3$ reaction was corrected. This resulted in 20% increase in this rate constant at 300^oK.
- The reaction of formaldehyde with HO2 was deleted from the mechanism because it is expected to be negligible under relevant atmospheric and environmental chamber conditions, and because it permitted removal of one intermediate species from the mechanism. This does not affect the condensed SAPRC07 mechanisms because this reaction was already removed from them.
- The rate constant expression for the reaction of OH radicals with methyl hydroperoxide was changed to that recommended by the NASA (2006) evaluation. This gives a 300^oK rate constant that is 35% higher than that previously used, which was from the IUPAC (2006) evaluation, but which was superceded by a new IUPAC (2007) recommendation that gives an even higher rate constant. The branching ratios for the two competing reactions was also changed slightly to be consistent with the NASA (2006) recommendation.
- The group additivity parameters used in the mechanism generation system to estimate rate constants for reactions of OH radicals with higher organic hydroperoxides were modified to be consistent with the revised rate constant and branching ratio used for OH + methyl hydroperoxide. The parameters used in the previous version of the mechanism were in error and were not consistent even with the previously used IUPAC (2006) rate constant for OH + methyl hydroperoxide. The revised group additivity parameters resulted in changes in the rate constants and the product distributions derived for the reactions of OH with the lumped higher hydroperoxide species ROOH, R6OOH and RAOOH, and the reaction of CL with RAOOH.
- Composition assignments were revised for several mixtures for consistency with the speciation database (Carter, 2008c), resulting in slight changes in reactivities calculated for these mixtures. The affected mixtures, listed in order of reactivity changes, were “isomers of ethylbenzene”,

"C10 alkenes", and "isomers of butylbenzene". The MIR changes caused by these reassignments these were 20%, 9%, and 3%, respectively.

The mechanism was re-evaluated against the chamber data and there were no significant changes to the fits and therefore no need to change any of the adjustable parameters. The detailed mechanisms for individual VOCs and the lumped VOC species used in the fixed parameter mechanisms were not changed, though because of the changes to the base mechanism some calculated reactivities changed. These changes were minor in the MIR scale (less than 4% for all compounds) but in a few cases there were changes of up to 30%in the lower NOx scales because the affected reactions become more important in low NOx conditions.

The ozone changes in the reactivity scenario calculations caused by the mechanism update are shown in Figure 3. It can be seen that the ozone changes are no more than ~1% if the comparisons are made on the basis of the same NO_x inputs[4]. In general the O_3 decreased because the major change was the increase in the $HO_2 + O_3$ rate constant, which consumes ozone. The change was the greatest in the lower NO_x scenarios because this reaction becomes more important as NO_x is reduced.

The report to the CARB documenting the SAPRC-07 mechanism and the MIR and other reactivity scale tabulations has been revised to reflect these changes (Carter, 2009), and is available at the SAPRC mechanism web site at http://www.cert.ucr.edu/~carter/SAPRC. This includes the reactivity scale tabulation and the other large tables that are available in electronic form. The report has an Appendix summarizing all the changes made to the mechanism and the report and reactivity scale to date (Carter, 2009).

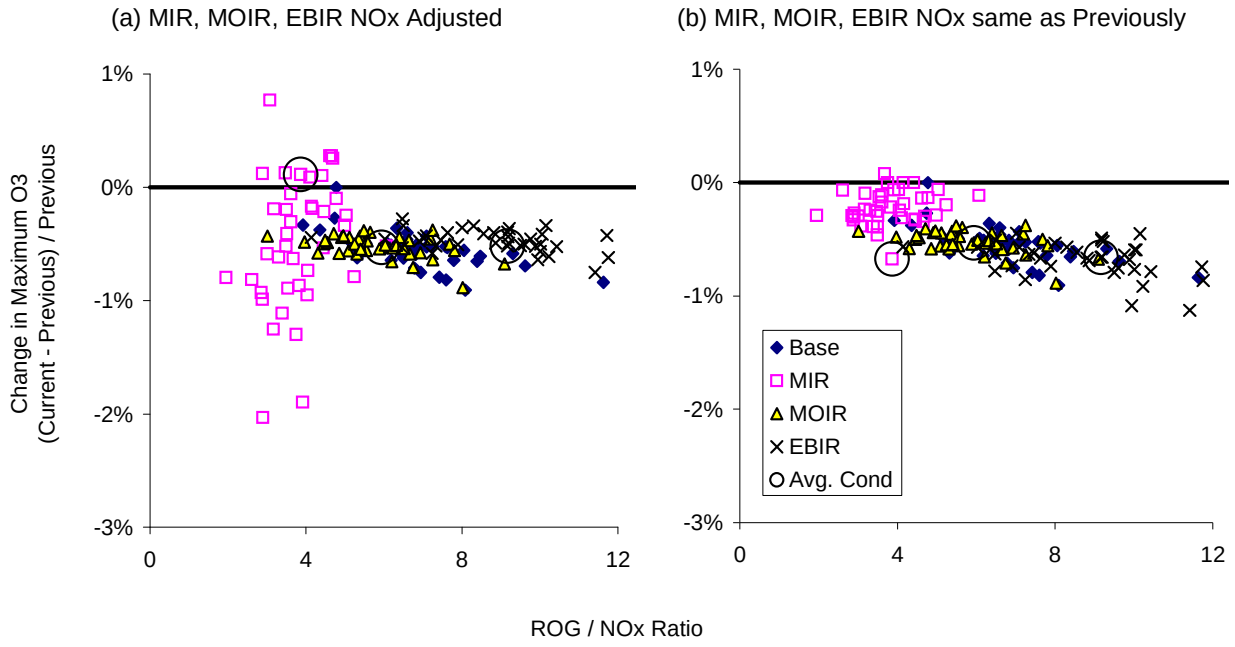

Figure 3. Relative changes in maximum ozone in the reactivity scenario calculations caused by the current SAPRC-07 mechanism updates.

[4] The initial NO_x in the MIR, MOIR, and EBIR scenarios depend on the mechanism because they are adjusted to set reactivity conditions, and therefore changed slightly when the mechanism was modified.

These changes to the base SAPRC-07 mechanism will result in corresponding changes being made to the condensed SAPRC07 mechanisms developed for the CARB and the "toxics" version of the mechanism being developed for the EPA. The latter mechanism contains additional OH + hydroperoxide reactions that will have to be changed as a result of this update. Because of time constraints it will not be possible to make these changes prior to the RSAC/RRAC meetings on March 25. It is also not possible to update all the files implementing the mechanisms for various modeling software systems that are available on the SAPRC mechanism web site. Every attempt will be made to complete these changes as soon as possible after the meeting, and upload the changes to the mechanism files and documentation to the SAPRC mechanism web site.

Note that no changes to emissions assignments had to be made as a result of these mechanism updates. Therefore, the SAPRC-07 emissions assignments on the current speciation database (Carter, 2008c) do not need to be modified.

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